

Thermochemistry of solutions of biochemical model compounds

6. α,ω -dicarboxylic acids, -diamines and -diols in aqueous solution

N. NICHOLS,^a R. SKÖLD, C. SPINK,^b and I. WADSÖ

Thermochemistry Laboratory, Chemical Center, University of Lund,
S-220 07 Lund, Sweden

Short title: Thermochemistry of solutions of α,ω -compounds

Proofs should be sent to:

Professor Ingemar Wadsö, Thermochemistry Laboratory, Chemical Center,
P.O.Box 740, S-220 07 Lund, Sweden

^a Present address: Perstorp AB, S-284 00 Perstorp, Sweden

^b Present address: Chemistry Department, State University of New York,
Cortland, N.Y., U.S.A.

Department of Biology, University of Illinois at Chicago
Chicago, Illinois 60607-7073

Dr. Robert E. Smith, Director
Department of Biology, University of Illinois at Chicago

The following information was obtained from the
Department of Biology, University of Illinois at Chicago

Department of Biology, University of Illinois at Chicago

Department of Biology, University of Illinois at Chicago

Department of Biology, University of Illinois at Chicago
Department of Biology, University of Illinois at Chicago
Department of Biology, University of Illinois at Chicago

Department of Biology, University of Illinois at Chicago

Department of Biology, University of Illinois at Chicago
Department of Biology, University of Illinois at Chicago
Department of Biology, University of Illinois at Chicago

Abstract

Enthalpies of solution at infinite dilution in water at 293.15, 298.15 and 303.15 K have been determined for the following compounds of the type $X-(CH_2)_n-X$: $n=2-5$ for $X=OH$, $n=2-4$ for $X=NH_2$ and $n=2$ and 3 for $X=COOH$. $\Delta C_{p,soln}^\infty$ values have been calculated. Using a drop calorimeter, heat capacities for the pure compounds at 298.15 K have been determined. Combining these values with the $\Delta C_{p,soln}^\infty$ values, partial molar heat capacities at infinite dilution, $C_{p,2}^\infty$, were obtained. $C_{p,2}^\infty$ values for 1,6-hexanediol, 1,4-butane- and 1,5-pentane-dicarboxylic acid were determined by measuring the heat capacities of their aqueous solutions at different solute concentrations.

1. Introduction

The present work is one of a continuing series of calorimetric investigations of the thermodynamic properties of aqueous solutions of simple organic compounds which may be looked upon as simple models for biochemical systems. The main purpose of these studies is to characterize the role of water-solute interactions. A particular emphasis has been to study the heat capacity properties of hydrocarbon groups in dilute aqueous solutions and the manner in which they are affected by branching and by the presence of different polar groups. Hydrocarbon groups have large excess heat capacities which are believed to be related to the structuring of the surrounding water. Such hydrophobic hydrations are important for the structural properties of biochemical macromolecules as well as for the formation of different kinds of complexes and aggregates between biochemical molecules.

Earlier work in this series dealt with simple carboxylic acids, amines, amides, and alcohols;^(1,2) ethylene glycol derivatives,⁽³⁾ benzene derivatives⁽⁴⁾ and amino acids.⁽⁵⁾ The present study deals with the solution properties of diols, diamines and dicarboxylic acids. Enthalpies of solution have been determined at different concentrations and temperatures from which $\Delta C_{p,\text{soln}}^\infty$ values have been derived. Heat capacities for the pure compounds, C_p^x , have also been determined, which in combination with the $\Delta C_{p,\text{soln}}^\infty$ values lead to partial molar heat capacities, $C_{p,2}^\infty$. For some compounds $C_{p,2}^\infty$ values were determined directly by heat capacity measurements of their aqueous solutions at different solute concentrations.

The present work is one of a continuing series of laboratory investigations of the thermodynamic properties of aqueous solutions of simple organic compounds which may be looked upon as simple models for biochemical systems. The main purpose of these studies is to characterize the roles of water-solute interactions. A particular emphasis has been to study the heat capacity properties of hydration groups in dilute aqueous solutions and the manner in which they are affected by hydrogen and hydrophobic bonding. The presence of different polar groups. Hydration groups have large extra heat capacities which are believed to be related to the structuring of the surrounding water. Such hydrophobic hydration is important for the structural properties of chemical macromolecules as well as for the formation of different kinds of complexes and aggregates between biomolecules.

Digitized by the Internet Archive
in 2026

Earlier work in this series has been published in the following papers: (1) *Heat capacities and enthalpies of dilution of aqueous solutions of simple organic compounds*, J. Chem. Phys. 19, 101 (1951); (2) *Heat capacities and enthalpies of dilution of aqueous solutions of simple organic compounds. II. The present study deals with the derivatives and limiting values*, J. Chem. Phys. 20, 101 (1952); (3) *Solution properties of diols, diamines and dicarboxylic acids*, J. Chem. Phys. 21, 101 (1953). Of solution have been determined at different concentrations and temperatures. Curves from which ΔG° values have been derived. Heat capacities for this component, C_p° , have also been determined, which in combination with the ΔG° values lead to partial molar heat capacities, C_p° . For some compounds C_p° values were determined directly from measurements of their aqueous solutions at different concentrations.

2. Experimental

MATERIALS

1,2-Ethanediol (Extra pure B.D.H. reagent grade) and 1,3-propanediol (B.D.H. reagent grade) were purified by drying with 4 Å molecular sieves followed by fractional distillation.

1,4-Butanediol (B.D.H. reagent grade) was frozen out twice at 18 °C and 1,6-hexanediol (Fluka purum quality) three times at 40 °C, while 1,5-pentanediol (Fluka AG puriss) was fractionally distilled prior to freezing out twice at -18 °C.

The diamines (Fluka AG puriss) were all fractionally distilled in a dry N₂-atmosphere.

All distillations have been performed at reduced pressures.

Glutaric and pimelic acid (Fluka AG purum) were purified by repeated crystallization from benzene (Merck p.a.). Acidimetric titration of these acids indicated their purities to be >99.5 mass per cent. Neither compound showed any trace of anhydride.⁽⁶⁾ The sample of succinic acid was described in reference 7. Adipic acid (Fluka purum quality, >99.5 mass per cent) was used as received.

Water contents were for the diols in all cases <0.03 and for the diamines <0.06 mass per cent, as determined by g.l.c. using a Porapak Q column and TC-detector. Assay for organic contaminants was also carried out by g.l.c. with a FID detector. No traces of impurities were found in the diols or the diamines using a silicon column. The diamines were further tested on a carbowax column with the same result. NMR investigation of the three lowest diols showed no detectable presence of isomeric products.

CALORIMETRY

Enthalpies of solution were determined by use of a modified LKB 8721-1 reaction and solution calorimeter.⁽⁸⁾ The calorimeter vessel, volume 100 cm³, is practically identical with that of the commercial instrument but a different method for thermistor measurements and data acquisition is employed. A constant current is passed through the thermistor and the resulting potential is partially compensated by a constant potential source. The net voltage is amplified and the signal is read by a 5 place digital voltmeter and is printed out each five seconds by use of a paper punch. Calculations were performed with a Hewlett Packard 9810A calculator equipped with a tape reader. The calorimeter was tested by use of the "tris"-test reaction leading to the values ΔH_{soln} (0.1 mol dm⁻³ HCl; 298.15 K) = $-(29.768 \pm 0.005)$ kJ mol⁻¹ and $\Delta C_{\text{p,soln}}$ (298.15 K) = (174.1 ± 0.8) J K⁻¹ mol⁻¹.

Heat capacities were measured for the pure compounds at 298.15 K by use of a precise double drop heat capacity calorimeter.⁽⁹⁾ For some of the substances this instrument was also used for direct measurements of the heat capacities of the aqueous solutions at different concentrations. The sample ampoule was charged with ca. 0.3 g of the solid compounds or with ca. 0.6 cm³ of the liquid substances or the aqueous solutions. The reference ampoule was empty. The calorimeter was calibrated with water. Specific heat capacity for water was taken to be 4.1797 J K⁻¹ g⁻¹.⁽¹⁰⁾

In order to avoid effects of ionization, the experiments with diamines were performed in 0.100 M NaOH and the dicarboxylic acids were dissolved in 0.100 M HCl.

Uncertainties given for $\Delta H_{\text{soln}}^{\infty}$ and C_{p}^{∞} are twice the standard deviation of the mean. Uncertainties in the partial specific heat capacities for

the drop calorimetric measurements are determined by the linear regression method⁽¹¹⁾ and errors in $\Delta C_{p,\text{soln}}^\infty$ and $C_{p,2}^\infty$ from the enthalpy of solution measurements are estimates.

3. Results

ENTHALPIES OF SOLUTION

In table 1 results of the solution calorimetric measurements are summarized. On the average five experiments were made for each compound and each temperature. Final concentrations were in the range 0.01 to 0.05 mol dm⁻³. For 1,6-hexanediol, 1,4-butanedicarboxylic acid and 1,5-pentanedicarboxylic acid solubilities were too low to allow satisfactory enthalpy of solution measurements. Enthalpy values at zero concentration, $\Delta H_{\text{soln}}^\infty$, were taken as the mean of the experimental values as no concentration dependency was found for any of the substances.

No precise measurements of the aqueous enthalpies of solution for except for succinic acid. the present series of compounds seem to have been made earlier / Corkill et al.⁽¹²⁾ have measured $\Delta H_{\text{soln}}^\infty$ (298.15 K) for several diols, HO(CH₂)_nOH; n=2-9. The agreement with the present results for n = 2-5 is fair.

HEAT CAPACITIES

Results from the $\Delta H_{\text{soln}}^\infty$ determinations were used to calculate the change in heat capacity in going from the pure compound to the infinitely dilute aqueous solutions, $\Delta C_{p,\text{soln}}^\infty$. The results for $\Delta H_{\text{soln}}^\infty$ were represented by the equation

$$\Delta H_{\text{soln}}^\infty = a + bT + c \cdot T^2 \quad (1)$$

and

$$\Delta C_{p,\text{soln}}^\infty = b + 2c \cdot T \quad (2)$$

Heat capacity values for the pure compounds, C_p^x , were combined with the corresponding $\Delta C_{p,\text{soln}}^\infty$ values to give the partial molar heat capacities, $C_{p,2}^\infty$

$$C_{p,2}^\infty = C_p^x + \Delta C_{p,\text{soln}}^\infty \quad (3)$$

The relationship between specific heat capacity, measured by the drop calorimeter, and the partial specific heat capacity is given by the equation⁽¹³⁾

$$(1 + W_2)c_p = c_{p,1} + W_2c_{p,2} \quad (4)$$

where W_2 is the weight ratio of solute to solvent, c_p is the measured specific heat capacity and $c_{p,1}$ and $c_{p,2}$ are the partial specific heat capacities for solvent and solute, respectively. Thus, from the slope of the plot $(1 + W_2)c_p$ versus W_2 the partial specific heat capacity of the solute could be calculated. W_2 was in the range 0.005 to 0.020. Values for C_p^x , $\Delta C_{p,2}^\infty$ and $C_{p,2}^\infty$ are summarized in table 2. Some $C_{p,2}^\infty$ values from other recent studies are also given.

For two of the dicarboxylic acids ($n=2,3$) both methods for the determination of $C_{p,2}^\infty$ were used. Within uncertainty limits the results are the same. The agreement between the present $C_{p,2}^\infty$ values and those obtained by other workers is fair, although there appears to be some systematic difference between our value for 1,4-butanediol and the very precise value recently determined by Jolicoeur and Lacroix⁽¹⁴⁾ (table 2).

Recently, Messerly et al.⁽¹⁵⁾ have reported C_p^x values for $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$ over a wide range of temperatures. Their value at 298.15 K, $172.59 \text{ J K}^{-1} \text{ mol}^{-1}$, is in excellent agreement with that reported here. Our C_p^x value for succinic acid is in good agreement with a value reported by Parks and Kelley,⁽¹⁶⁾ $151 \text{ J K}^{-1} \text{ mol}^{-1}$.

In connection with the drop heat capacity measurements of the solutions of dicarboxylic acids, measurements were also made on the pure solution of HCl, $c = 0.100 \text{ mol dm}^{-3}$. The obtained value for the specific heat capacity, $c_p = (4.1534 \pm 0.0004) \text{ J K}^{-1} \text{ g}^{-1}$, is significantly higher than the value which may be derived from the apparent molal heat capacity data given in reference 17, $c_p = 4.1517 \text{ J K}^{-1} \text{ g}^{-1}$.

4. Discussion

Values for aqueous enthalpies of solution refer to very complex processes and can usually not be discussed in any detail at the present time. Enthalpy values for the transfer process from the gaseous state to infinite dilute solution are usually more rewarding to examine but for the series of compounds investigated here accurate enthalpy of vaporization values are not yet available.

For a solution process the $\Delta C_{p,\text{soln}}^\infty$ values reflect the properties of the pure compounds as well as those of the solvated compound and the resultant effect on the solvent structure. The $C_{p,2}^\infty$ values, however, do not contain any contributions due to interactions in the pure compound and therefore may be considered directly to reflect solute - solvent interactions.

For the series of compounds investigated earlier⁽¹⁻⁵⁾ it was found that $C_{p,2}^\infty$ values for each series can be accurately expressed by the equation

$$C_{p,2}^\infty = a + bn \quad (5)$$

where a and b are constants and n is the number of alkyl carbon groups. For the different series a has values rather close to that of the parent compound ($n=0$). The value for b , which is the CH_2 increment for straight

chain compounds, was in most cases found to be close to $90 \text{ J K}^{-1} \text{ mol}^{-1}$.⁽¹⁸⁾

For the short series of phenyl derivatives⁽⁴⁾ and alkyl amino acids⁽⁵⁾ b values were found to be lower, ca. 70 and $80 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

The diamines and dicarboxylic acids were measured in the presence of NaOH and HCl, respectively, $c = 0.100 \text{ mol dm}^{-3}$. This electrolyte concentration is not believed to significantly affect the $C_{p,2}^{\infty}$ values; it was earlier shown⁽⁴⁾ that the presence of NaCl does not influence aqueous $C_{p,2}^{\infty}$ values for $\text{EtOCH}_2\text{CH}_2\text{OH}$ and $\text{PhOCH}_2\text{CH}_2\text{OH}$ for $c \leq 0.5 \text{ mol dm}^{-3}$. Further, normal CH_2 -increments ($\sim 89 \text{ J K}^{-1} \text{ mol}^{-1}$) were found for RNH_2 and RCOOH ⁽¹⁾ which also were measured in the presence of NaOH and HCl, respectively.

For the present series of compounds we note a substantial deviation from linearity when $C_{p,2}^{\infty}$ values are plotted versus n , figure 1. The curves represent second degree least squares equations fitted to the experimental values. The dotted lines, slope $89 \text{ J K}^{-1} \text{ mol}^{-1}$, represent the normal CH_2 increments found for monofunctional compounds.⁽¹⁸⁾

For all series the slopes of the curves appear to approach the normal value. For the diol series the CH_2 increments are in fact within uncertainty limits equal to the normal value except for that between $n=2$ and 3. It is interesting to note that the value for the diols extrapolated to $n=0$ is $47 \text{ J K}^{-1} \text{ mol}^{-1}$. This value is very close to the $C_{p,2}^{\infty}$ value which may be derived for hydrogen peroxide,⁽¹⁹⁾ $52 \text{ J K}^{-1} \text{ mol}^{-1}$.

The non-linearity observed for the present series of compounds, in particular for the dicarboxylic acids, is believed to reflect characteristic structural features for these compounds in aqueous solution. It could possibly be an effect of temperature dependent equilibria, e.g. the breaking of intramolecular hydrogen bonds.

The authors are grateful to Professor Vanderzee for the gift of the sample of succinic acid and to Drs. Jolicoeur and Lacroix for making their manuscript available to us prior to its publication.

This work has been supported by grants from the Swedish Board for Technical Development and the Swedish Natural Science Research Council. N.N. acknowledges a NATO fellowship held during this work.

REFERENCES

1. Konicek, J.; Wadsö, I. *Acta Chem. Scand.* 1971, 25, 1541.
2. Öjelund, G.; Sköld, R.; Wadsö, I. *J. Chem. Thermodynamics* 1976, 8, 45.
3. Kusano, K.; Suurkuusk, J.; Wadsö, I. *J. Chem. Thermodynamics* 1973, 5, 757.
4. Nichols, N.; Wadsö, I. *J. Chem. Thermodynamics* 1975, 7, 329.
5. Spink, C.; Wadsö, I. *J. Chem. Thermodynamics* 1975, 7, 561.
6. Feigl, F. *Spot tests. Volume II: Organic Applications.*
Elsevier Publishing Co.: Amsterdam. 1954, p. 174.
7. Vanderzee, C.E.; Westrum, Jr., E.F. *J. Chem. Thermodynamics* 1970, 2, 681.
8. Nichols, N.; Sköld, R.; Wadsö, I. *Chemica Scripta.* In press.
9. Suurkuusk, J.; Wadsö, I. *J. Chem. Thermodynamics* 1974, 6, 667.
10. Osborne, N.S.; Stimson, H.F.; Ginnings, D.C. *J. Res. Natl. Bur. Stand.* 1939, 23, 197.
11. Lark, P.D.; Craven, B.R.; Bosworth, R.C.L. *The Handling of Chemical Data.* Pergamon: Oxford. 1968, p. 136.
12. Corkill, J.M.; Goodman, J.F.; Tate, J.R.
Trans. Faraday Soc. 1969, 65, 1742.
13. Bull, H.B.; Breeze, K. *Arch. Biochem. Biophys.* 1968, 128, 497.
14. Jolicoeur, C.; Lacroix, G. *Can. J. Chem.* In press.
15. Messerly, J.F.; Finke, H.L.; Osborn, A.G.; Douslin, D.R.
J. Chem. Thermodynamics 1975, 7, 1029.
16. Parks, G.S.; Kelley, K.K. *J. Amer. Chem. Soc.* 1925, 47, 2089.
17. Parker, V.B. *Thermal Properties of Aqueous Uni-valent Electrolytes.*
National Bureau of Standards, NSRDS-2. 1965.

18. Nichols, N.; Sköld, R.; Spink, C.; Suurkuusk, J.; Wadsö, I.
To be published.
19. Giguère, P.A.; Morissette, B.G.; Olmos, A.W.; Knop, O.
Can. J. Chem. 1955, 33, 804.
20. Kawaizumi, F.; Otake, T.; Nomura, H.; Miyahara, Y.
Nippon Kagaku Kaishi 1972, 10, 1772.
21. Vanderzee, C.E.; Månsson, M.; Wadsö, I.; Sunner, S.
J. Chem. Thermodynamics 1972, 4, 541.

TABLE 1. Enthalpies of solution in water at infinite dilution, $\Delta H_{\text{soln}}^{\infty}$, for some diols, diamines and dicarboxylic acids.

Substance	$\Delta H_{\text{soln}}^{\infty} / \text{kJ mol}^{-1}$		
	293.15K	298.15K	303.15K
$\text{HO}-(\text{CH}_2)_2-\text{OH}$	-7.06 ± 0.02	-6.87 ± 0.02	-6.62 ± 0.01
$\text{HO}-(\text{CH}_2)_3-\text{OH}$	-9.11 ± 0.02	-8.67 ± 0.02	-8.19 ± 0.02
$\text{HO}-(\text{CH}_2)_4-\text{OH}$	-11.18 ± 0.01	-10.46 ± 0.01	-9.69 ± 0.03
$\text{HO}-(\text{CH}_2)_5-\text{OH}$	-11.66 ± 0.03	-10.59 ± 0.01	-9.60 ± 0.02
$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2^{\text{a}}$	-31.80 ± 0.01	-31.78 ± 0.01	-31.68 ± 0.01
$\text{H}_2\text{N}-(\text{CH}_2)_3-\text{NH}_2^{\text{a}}$	-35.80 ± 0.01	-35.62 ± 0.03	-35.27 ± 0.02
$\text{H}_2\text{N}-(\text{CH}_2)_4-\text{NH}_2^{\text{a}}$	-37.04 ± 0.02	-36.60 ± 0.02	-36.00 ± 0.02
$\text{HOOC}-(\text{CH}_2)_2-\text{COOH}^{\text{b}}$	28.39 ± 0.03	$28.71 \pm 0.02^{\text{c}}$	29.14 ± 0.04
$\text{HOOC}-(\text{CH}_2)_3-\text{COOH}^{\text{b}}$	24.65 ± 0.04	25.09 ± 0.01	25.67 ± 0.02

^a Values refer to dilute NaOH solution, $c = 0.100 \text{ mol dm}^{-3}$.

^b Values refer to dilute HCl solution, $c = 0.100 \text{ mol dm}^{-3}$.

^c Vanderzee et al.⁽²¹⁾ have earlier reported the value $28.70 \pm 0.03 \text{ kJ mol}^{-1}$.

TABLE 2. Heat capacity values for some diols, diamines and dicarboxylic acids at 298.15 K. $C_p^\ddagger$ is the molar heat capacity for the pure compounds, $\Delta C_{p,\text{soln}}^\infty$ is the heat capacity change for the aqueous solution process and $C_{p,2}^\infty$ is the corresponding partial molar heat capacity in the infinitely dilute aqueous solution .

Substance	$C_p^\ddagger/J\ K^{-1}\ mol^{-1}$	$\Delta C_{p,\text{soln}}^\infty/J\ K^{-1}\ mol^{-1}$	This work	$C_{p,2}^\infty/J\ K^{-1}\ mol^{-1}$	Literature
$HO-(CH_2)_2-OH$	149.7 ± 0.1	43 ± 2	193 ± 2		191.9 ± 0.1^a , 201 ^b
$HO-(CH_2)_3-OH$	176.4 ± 0.1	93 ± 4	269 ± 4		263 ^b
$HO-(CH_2)_4-OH$	204.2 ± 0.1	150 ± 3	354 ± 3		346.8 ± 0.3^a
$HO-(CH_2)_5-OH$	233.2 ± 0.2	206 ± 6	439 ± 6		
$HO-(CH_2)_6-OH$			528 ± 8^c		521.6 ± 0.2^a
$H_2N-(CH_2)_2-NH_2$	172.6 ± 0.1	12 ± 2^d	185 ± 2^d		
$H_2N-(CH_2)_3-NH_2$	203.8 ± 0.2	52 ± 3^d	256 ± 3^d		
$H_2N-(CH_2)_4-NH_2$	236.3 ± 0.2	104 ± 4^d	340 ± 4^d		
$HOOC-(CH_2)_2-COOH$	153.6 ± 0.2	75 ± 6^e	229 ± 6^e $223 \pm 5^{c,e}$	225 ± 4^f	
$HOOC-(CH_2)_3-COOH$	174.4 ± 0.4	103 ± 6^e	277 ± 6^e $267 \pm 5^{c,e}$	271 ± 4^f	
$HOOC-(CH_2)_4-COOH$	195.9 ± 0.3		$336 \pm 10^{c,e}$		
$HOOC-(CH_2)_5-COOH$	217.7 ± 0.5		$410 \pm 5^{c,e}$		Cont.

TABLE 2. Cont.

^a Reference 14

^b Reference 20, 303.15 K

^c Measured directly with drop heat capacity calorimeter

^d Values refer to dilute NaOH solution, $c = 0.100 \text{ mol dm}^{-3}$

^e Values refer to dilute HCl solution, $c = 0.100 \text{ mol dm}^{-3}$

^f Weighted mean values

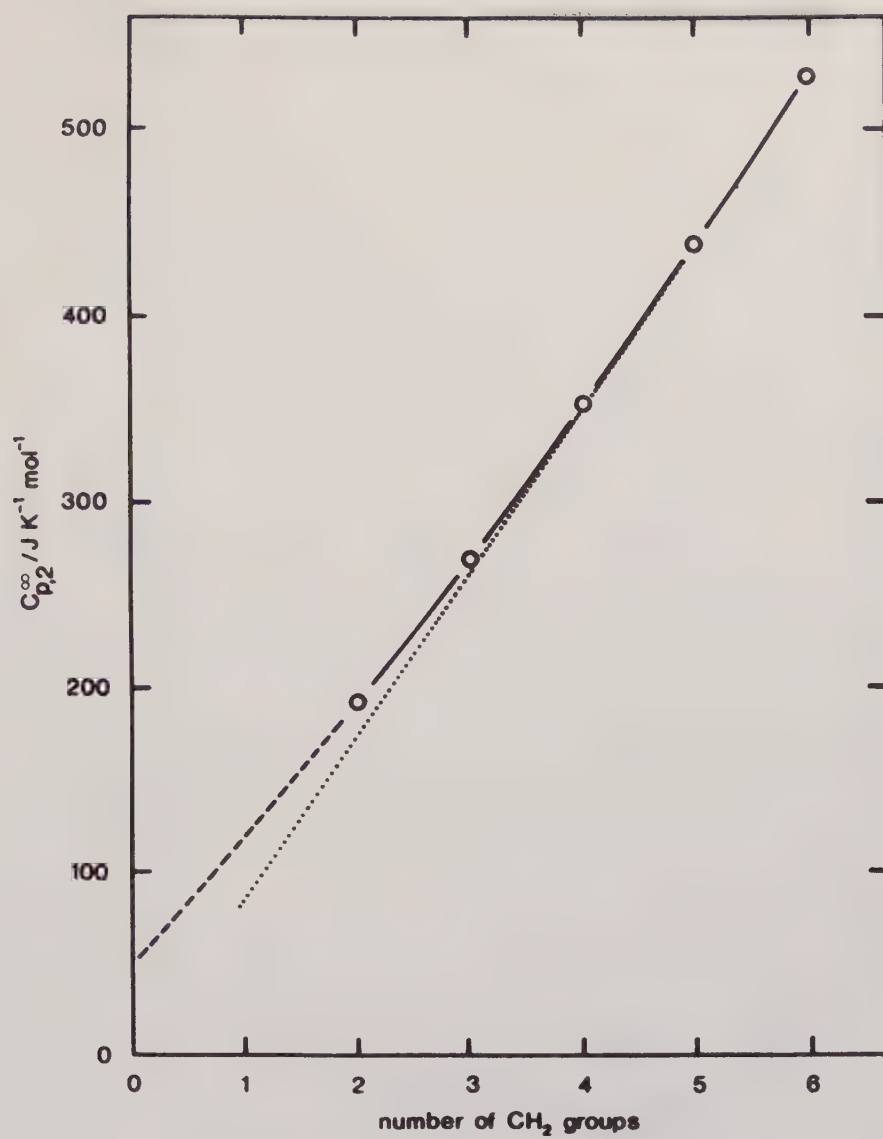


Figure 1:(a)

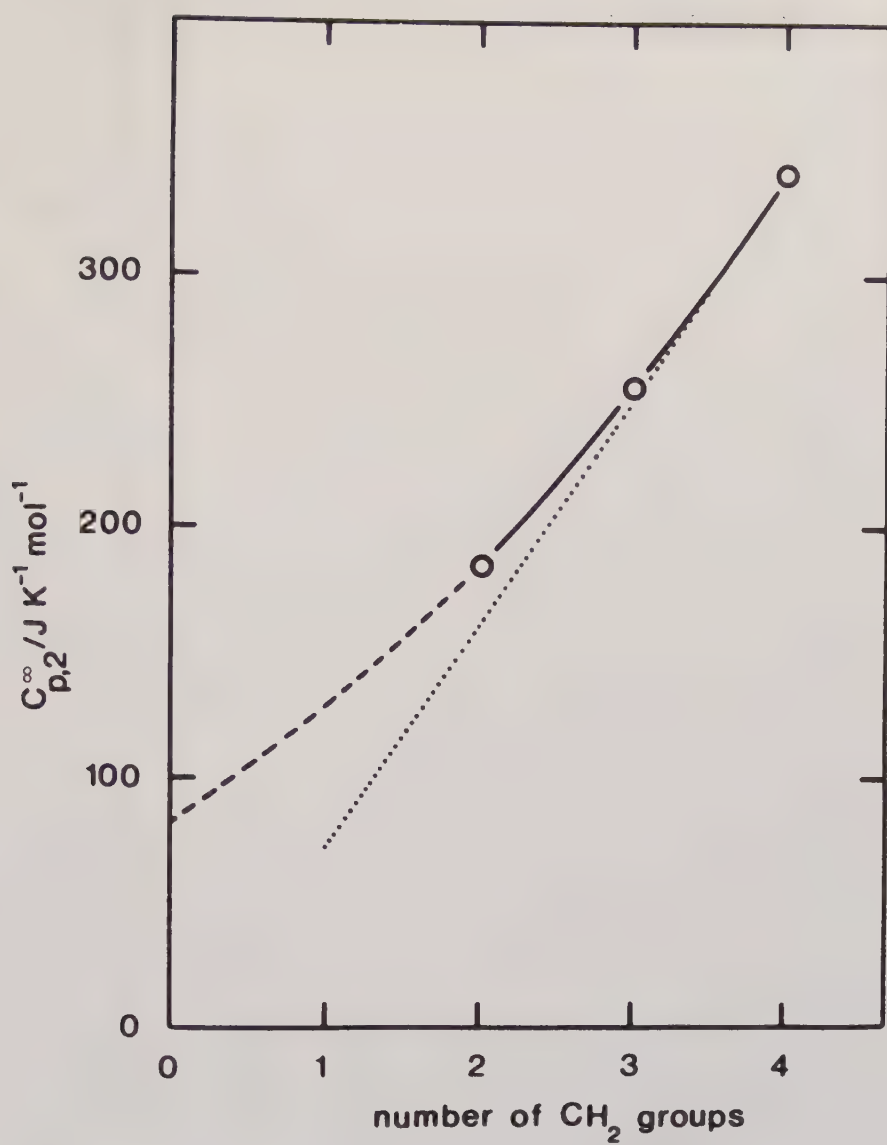


Figure 1:(b)

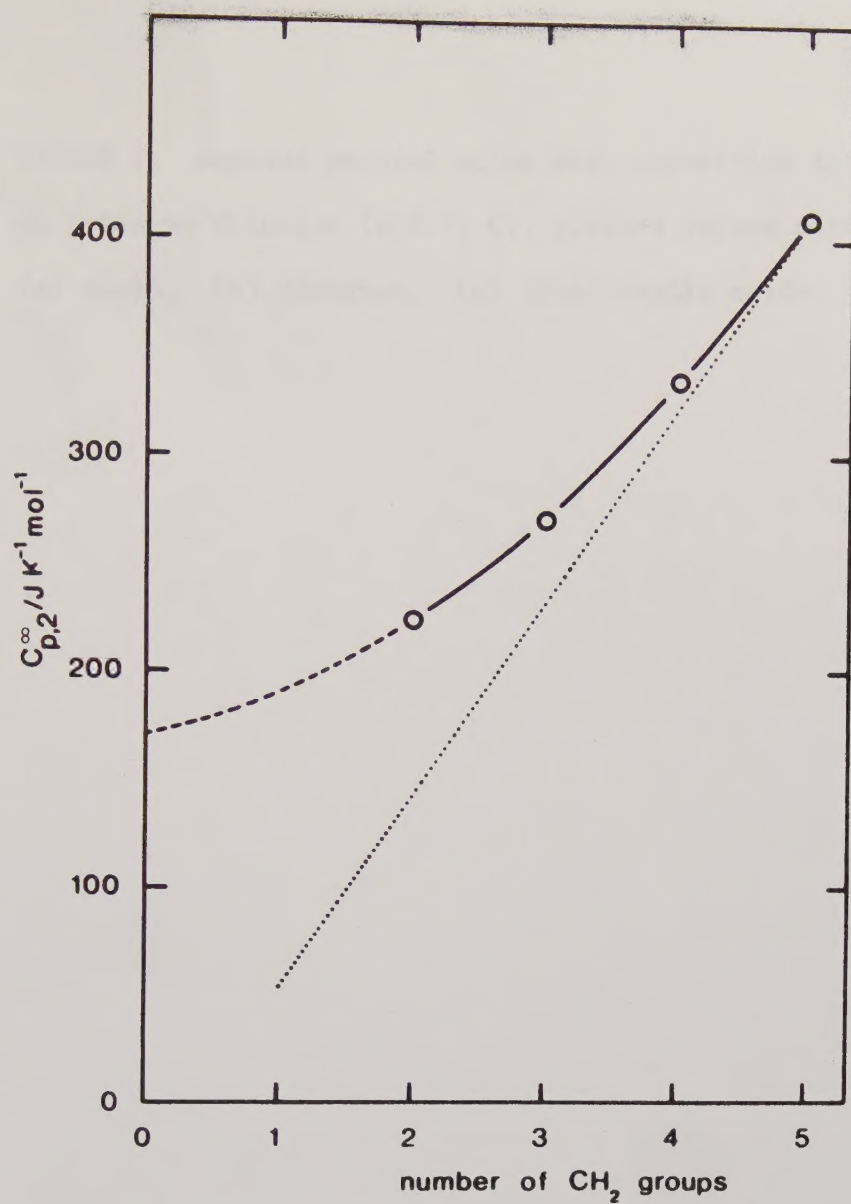


Figure 1:(c)

Figure legend

FIGURE 1. Aqueous partial molar heat capacities for some α,ω -compounds at infinite dilution (298.15 K), plotted versus number of CH_2 -groups: (a) diols, (b) diamines, (c) dicarboxylic acids.

